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(54) Title: DETERGENT COMPOSITION CONTAINING AN ENZYME AND A GLYCOSIDE SURFACTANT

(57) Abstract

Detergent compositions are obtained through the combination of glycoside surfactants and an enzyme.

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# DETERGENT COMPOSITION CONTAINING AN ENZYME AND A GLYCOSIDE SURFACTANT

## BACKGROUND OF THE INVENTION

1. Field of the Invention.

This invention relates to detergent products particularly those for laundry uses.

2. Description of the art.

Enzymes have long been used in the detergent arts to enhance the cleaning of fabrics. Specific stains on soiled fabrics are particularly responsive to enzymes which cleave specific linkages in the molecules of the stain. For instance, proteases and lipases are effective on stains such as blood or oils. These stains are protein fractions from food and fats such as are deposited from body soil. The action of the enzyme on the particular stain assists the surfactant to render overall cleaning improvement. For instance, U. S. Patent 4,011,169 issued on March 8, 1977 to Diehl et al, "Enzyme Containing Compositions Containing Aminated Polysaccharides" discloses detergent products containing enzymes.

The use of enzymes with anionic surfactants such as alpha olefin sulfonates is disclosed in U. S. Patent 4,272,396 issued June 9, 1981 to Fukano.

The use of glycosides in detergent compositions is disclosed in U. S. Patent 4,446,042 issued May 1, 1984 to Leslie. Further glycoside materials are described in Mansfield U. S. Patent 3,640,998 issued February 8, 1972. A method of manufacturing glycosides is found in Roth U. S. Patent 4,223,129 issued September 6, 1980.

A particular difficulty in working with enzymes is that when they are presented in the form of powders,

there have been instances of sensitization to the enzyme in selected individuals. To avoid contact with the enzymes, it has been proposed that the detergent products containing the same be prepared in the form of a liquid thus minimizing any dust containing the enzyme. However, liquid detergent formulations containing enzymes lead to problems in the stability in the enzyme. The problem of placing the enzymes in a liquid environment is that as organic materials, they are subject to bacterial growth and inactivation. It is therefore a problem to stabilize enzymes over long periods of time, particularly when they are exposed to heat which aggravates the enzyme stability.

The effect of various surfactants on enzyme stability is found in a paper entitled Effect of Surfactant Structure On Stability Of Enzymes Formulated Into Laundry Liquids by Kravetz et al which contains a presentation date of May 1984 - 75th Annual Meeting AOCS.

It therefore is desirable to obtain a detergent product in a liquid or solid form in which the enzyme is stabilized such that synergistic cleaning results are obtained. The present invention deals with laundry detergent products in which the effect of the enzyme is enhanced by the inclusion of a glycoside surfactant.

Throughout the specification and claims, percentages and ratios are by weight, temperatures are in degrees Celsius and pressures are in KPascals over ambient unless otherwise indicated. The references cited in this patent are, to the extent applicable, herein incorporated by reference.

## SUMMARY OF THE COMPOSITION OF THE INVENTION

A detergent composition is described comprising:

(a) from about 1% to about 70% by weight of a glycoside surfactant;

(b) from about 0.005% to about 5% by weight of an enzyme; and

(c) from about 5% to abut 80% by weight of a member selected from the group consisting of water, lower alcohols, glycols, detergent builders and mixtures thereof.

## DETAILED DESCRIPTION OF THE INVENTION

It has now been found that through the use of a glycoside surfactant that improved laundry cleaning results can be obtained with enzymes. In particular, protease enzymes are utilized with great effect in the present invention. Other enzymes such as alcalases may also be utilized as well.

The glycosides with which the present invention are presently concerned are conveniently represented by the formula:

$$R(OG)_x$$

where R is an organic hydrophobic residue typically alkyl and having from 10 to 20 carbon atoms in the alkyl group. The alkyl group may also be substituted such as with a hydroxyl group or may include an alkoxy group between the hydrophobic residue and the saccharide. However, the preferred hydrophobic residue is a straight chain alkyl. O is an oxygen atom and provides the linkage (ordinarily formed through an acetal mechanism) between the alkanol which is the basis of the alkyl group in the glycoside and the saccharide.

Typically, the saccharides employed herein are fructose, glucose, mannose, galactose, talose, gulose, allose, altrose, idose, arabinose, xylose, lyxose and ribose. Preferably, the glycoside is formed from glucose units.

In the above-described formula, the degree of polymerization (DP) is determined as an average value from the number represented by x. The value of x which is an average varies between about 1.2 and about

8; typically about 1.3 to about 5 and preferably about 1.4 to about 3.0.

The glycosides utilized herein may be prepared according to the process described in U. S. Patent 4,223,129 issued September 6, 1980 to Roth et al. The source of the glycoside is not however crucial to the present invention therefore any commercial source of the glycoside may be utilized. In addition to the basic glycosides, materials containing alkoxy group such as ethylene or propylene oxide pendant from the saccharide may be used. Such materials are described in pending United States patent application serial number 06/704,828 filed February 22, 1985 by Roth et al. (a copy of which is in the file of the present application).

The enzymes which are utilized herein are most often proteases although alcalase, lipase, tannase, and esterase may be employed in the present invention either alone or in combination with one another. The enzymes utilized herein include the following materials.

Lipases suitable for use herein include those of animal, plant, and microbiological origin. Although only a few studies on lipase distribution in plants have been conducted, suitable lipase enzymes are present in cambium, bark, and in plant roots. In addition, lipases have been found in the seeds of fruit, oil palm, lettuce, rice, bran, barley and malt, wheat, oats and oat flour, cotton tung kernels, corn, millet, coconuts, walnuts, fusarium, cannabis and cucurbito.

Suitable lipases are also found in many strains of bacteria and fungi. For example, lipases suitable for use herein can be derived from Pseudomonas, Aspergillus, Pneumococcus, Staphylococcus, and

Staphylococcus Toxins, Mycobacterium Tuberculosis, Mycotorula Lipolytica and Sclerotinia microorganisms.

Suitable animal lipases are found in the body fluids and organs of many species. Most organs of mammals contain lipases, but in addition, the enzymes are found in several digestive juices as well as in pancreatic juice. A preferred class of animal lipase herein is the pancreatic lipase.

Specific examples of the commercially available lipase enzymes, suitable for use herein, the pH ranges of their optimum activity, and the source appear in Table I. Of course, it is preferred to use a given lipase with its range of optimum activity.

TABLE I

| *Lipase | PH Range of Lipolytic Activity | Source |
|---|---|---|
| Remyzyme PL-600 | 7-11 | Pancreatic Juice |
| Astra | 7-10 | Microbial |
| Nacase | 7-9 | Microbial |
| Lipase YL | 7-9 | Microbial |
| Wallerstein AW | 7-9 | Fungal |
| Amano M-AP | 6-8 | Fungal |
| Meito MY-30 | 6-8 | Fungal |
| Amano CE | 8-10 | Microbial |
| Amano CE-50 | 7-10 | Microbial |
| Amano AP-6 | 6-8 | Fungal |
| Takedo 1969-4-9 | 6-8 | Microbial |

*Designated by commercial source.

The lipases preferred for use herein are Amano CE, Amano M-AP, Takedo 1969-4-9, and Meito MY-30.

Lipases can be employed in the present detergent compositions in an amount from about 0.005% to about 5%, preferably from 0.01% to 2.5%, on a pure enzyme basis. While in the wash liquor, the concentrations employed are dependent upon the particular enzyme used and the conditions of solution, such as pH, temperature, and period of the pre-soak, if any. Normally, concentrations of enzyme in the range of from about 1 ppm to about 100 ppm, and preferably from about 5 ppm to about 500 ppm, are employed. Pre-soak compositions having a lipase component within the range defined hereinbefore normally provides useful concentrations of lipase in solution.

The amylolytic enzymes which can be stabilized and enhanced in the detergent composition embodiment can be of fungal, plant, animal or bacterial origin. Suitable amylolytic enzymes include alpha and beta amylases. By way of example, suitable alpha-amylases of mold origin including those derived from Aspergillus oryzae, Aspergillus niger, Aspergillus alliaceus, Aspergillus wentii, and Pencillium glaucum. The alpha-amylases derived from cereal grains, pancreatic sources and such bacteria as Bacillus subtilis, Bacillus macerans, Bacillus mesentericus and Bacillus thermophilus are also useful herein. These enzymes are active in the pH range of from about 4.5 to about 12 and, depending upon the species, at temperatures including laundering temperatures, i.e., 35°C up to the boil.

Preferred amylolytic enzymes herein are the alpha-amylases derived from the bacterial organism Bacillus subtilis. These amylases provide excellent desizing and starch digestive properties and are especially useful in the laundering of textile materials containing soils and stains of a starchy nature.

The amylolytic enzymes useful herein can be employed in a pure state. Generally, they are employed in the form of a powdered commercially available preparation wherein the amylolytic enzyme is present in an amount of from about 2 to about 80% of the preparation. The remaining portion, i.e., about 20% to about 98%, comprises inert vehicle such as sodium sulfate, calcium sulfate, sodium chloride, clay or the like. The active enzyme content of these commercial enzyme compositions is the result of manufacturing methods employed and is

not critical herein so long as the finished compositions of this invention have the hereinafter specified enzyme content. Specific examples of commercial enzyme preparations suitable for use herein and the manufacturers thereof include: Diasmen alpha-amylase (Daiwa Kasei KK, Tokyo, Japan); Rapidase alpha-amylase THC-25 (Rapidase, Seclin, France); Novo Bacterial alpha-amylase (Novo Industri, Copenhagen, Denmark); Wallerstein alpha-amylase (Wallerstein Company, Staten Island, New York); Rhozyme-33 and Rhozyme H-39 (Rohm & Haas, Philadelphia, Pennsylvania).

Preferred herein as a powdered enzyme preparation containing alpha-amylase and a mixture of alkaline and neutral proteases.available CRD-Protease (or Monsanto DA-10) from Monsanto Company, St. Louis, Missouri.

The amylolytic enzymes can be employed in the detergent composition embodiment of this invention in an amount from about 0.005% to about 5%, preferably from 0.01% to 2.5% on a pure enzyme basis.

Suitable proteolytic enzymes for use in the detergent composition embodiment can be of vegetable, animal bacterial, mold and fungal origin.

The proteolytic enzyme can be employed in the compositions of the present invention in an amount of 0.005% to about 5%, preferably 0.01% to 2.5% on a pure enzyme basis. Best results in terms of overall cleaning efficacy and stain-removing properties are attained when the proteolytic enzyme is employed in an amount of about 0.01% to about 1% on a pure enzyme basis.

Specific examples of proteases suitable for use are trypsin, collagenase, keratinase, elastase, subtilisin, BPN and BPN'. Preferred proteases are serine proteases produced from microorganisms such as bacteria, fungi or mold. The serine proteases which are procured by mammalian systems, e.g., pancreatin, are also useful herein.

Specific examples of commercial enzyme products and the manufacturer thereof include: Alcalase, Novo Industri, Copenhagen, Denmark; Maxatase, Koninklijke Nederlandsche Gist-En Spiritusfabriek N.V., Delft, Netherlands; Protease B-4000 and Protease AP, Schweizerische Ferment A.G., Basel, Switzerland; CRD-Protease, Monsanto Company, St. Louis, Missouri; Viokase, VioBin Corporation, Monticello, Illinois; Pronase-P, Pronase-E, Pronase-AS and Pronase-AF all of which are manufactured by Kaken Chemical Company, Japan; Rapidase P-2000, Rapidase Seclin, France; Takamine, HT proteolytic enzyme 200, Enzyme L-W (derived from fungi rather than bacteria), Miles Chemical Company, Elkhart, Indiana; Rhozyme P-11 concentrate, Rohzyme PF, Rhosyme J-25, Rohm & Haas, Philadelphia, Pennsylvania (Rhozyme PF and J-25 have salt and corn starch vehicles and are proteases having diastase activity); Amprozyme 200, Jacques Wolf & Company, a subsidiary of Nopco Chemical Company, Newark, New Jersey; Takeda Fungal Alkaline Protease, Takeda Chemical Industries, Ltd., Osaka, Japan; Wallerstein 201-HA, Wallerstein Company, Staten Island, New York; Protin AS-20, Dawai Kasei K.K., Osaka Japan; and Protease TP (derived from thermophilic Streptomyces

species strain 1689), Central Research Institute of Kikkoman Shoya, Noda Chiba, Japan.

The glycoside surfactant as previously discussed, is employed in the present invention at an amount from about 1% to about 70%; preferably from about 5% to about 65% and most preferably from about 10% to about 55% by weight of the total composition. The enzymes employed herein are included in the composition at from about 0.005% to about 5%; preferably from about 0.01% to about 5% by weight of the composition. The remainder of the composition at from about 5% to about 80%; preferably from about 10% to about 75%; most preferably from about 20% to about 60% by weight of the total composition is a member selected from the group consisting of water, lower alcohols, glycols, detergent builders and mixtures thereof.

The water is included herein as the preferred embodiment of the invention gives an aqueous based liquid product thereby minimizing the potential of allergic reactions to susceptible consumers. The lower alcohols and glycols are respectively materials which may be utilized to thin the composition and to stabilize the enzyme within the composition. For instance, propylene glycol is an excellent enzyme stabilizer and may be easily incorporated within the present invention. The lower alcohols include methanol, ethanol, normal propyl, isopropyl and mixtures thereof.

The detergent builders which may be incorporated within the present invention include all matter of normally utilized detergent builders such as orthophosphates, pyrophosphates, higher polymeric phosphates

such as tripolyphosphate, carbonates, citrates, organic builders including those described in pending U. S. Patent application 06/664,451 to Valenty filed October 23, 1984 (equivalent to EP-A-150930) and aluminolsilicates. Preferably, the water soluble materials included in the foregoing description are utilized in the form of their sodium, potassium, or ammonium salts. Where the organic to water ratio content of the detergent product is particularly high, it is often preferred to utilize the potassium salts because of their enhanced solubility.

Additional materials which may be included within the present invention are anionic cosurfactants. The anionic cosurfactants are conveniently selected from the group consisting of alkyl sulfates, alkyl ethersulfates, olefin sulfonates, paraffin sulfonates, alkylbenzene sulfonates, and mixtures thereof. In the foregoing compounds, the hydrophobic portion is usually obtained from an alcohol which varies between about 10 and about 20 carbon atoms; preferably from about 12 to about 18 carbon atoms. The anionic cosurfactants are conveniently formulated such that the cationic portion of the cosurfactant is selected from the group consisting of sodium, potassium or ammonium or mixtures thereof. The anionic cosurfactant is typically used in an amount of from about 3% to about 40%; preferably from about 5% to about 35% by weight.

The present invention also allows for the inclusion of nonionic cosurfactants. Typically, the nonionic cosurfactant will be an ethoxylated alcohol or an ethoxylated alkylphenyl. The hydrophobic (alkyl) portion of the nonionic cosurfactants are typically from

about 10 to about 20 carbon atoms; preferably from about 12 to about 18 carbon atoms in length. The amount of nonionic co-surfactant employed in the present invention is typically from about 5% to about 40%; preferably from about 7% to about 35% by weight.

A further variable from the present invention is the inclusion of a cationic surfactant. The cationic surfactants used in the composition of the present invention are preferably those containing two long carbon chains in conjunction with a quaternary ammonium group. Preferably the two long chains contain an average from about 12 to about 22, preferably from about 16 to 22, more preferably from about 16 to about 18 carbon atoms in each group. The remaining groups, if any, are attached to the quaternary nitrogen atom are preferably a $C_1$ to $C_4$ alkyl or hydroxy alkyl group. These chains can contain hydroxy groups or heteroatoms or other linkages, such as double or triple carbon-carbon bonds, ester, amide, or ether linkages. However, it is preferred that the long chains be alkyl groups.

The amount of the cationic surfactants when included in the present invention are typically at a level from about 1% to about 30%; preferably from about 2% to about 20% by weight of the total composition. Suitable cationic surfactants are described in U. S. Patent 4,493,773 to Cook et al issued January 15, 1985 which is incorporated herein by reference.

The detergent composition of the present invention are typically used at a solids concentration in the wash liquor at from about 0.01% to about 1.0% by

weight. The lower percentage of use for the product is typical in American washes which are done on a dilute basis while the higher surfactant concentrations are typical of the European boil wash systems. Other laundry additives may also be included in the compositions described herein such as optical brighteners, dyes, bleaches and the like. The product is preferably a pourable liquid but may be formulated as a granule or other solid form.

The following are suggested exemplifications of the present invention.

EXAMPLE I

A surfactant product is prepared according to the present invention by introducing a protease (alcalase 2.5L from NOVO) at a level of 1 part with an alkylpolyglucoside (alkyl 12-13 carbons) having an average DP of 3.0 at 32 parts together with 67 parts of water.

This product is found to clean clothes effectively when used at a wash concentration level of the surfactant present at 0.15% by weight in water under wash conditions of 37°C.

EXAMPLE II

A series of comparative examples is run showing the effect of the alkylpolyglycoside in enhancing the effectiveness of the enzyme utilized in a laundry detergent product.

The tests in the table below were run on EMPA 116 cotton fabric swatches with the total surfactant level at 1.4925 grams/l with enzymes at 0.0075 grams/l and the wash temperature at 49°C with the water hardness of 150 ppm calculated as calcium carbonate. The wash solution pH is adjusted to 8.0 using sodium bicarbonate.

The following definitions are applied:

APG is an alkyl polyglucoside with a hydrophobic portion of the molecule is between 12 and 13 carbon atoms long and the DP of the product is 3.

The abbreviation LAE is a linear alcohol ethoxylate having an average degree of ethoxylation of 7 and a carbon atom chain length of between 12 and 15 carbon atoms (NEODOL 25-7 from Shell)

The abbreviation LAES is a linear alcohol ethoxysulfate sodium salt where the number of ethoxy units is 3 and the carbon chain length of the surfactant is 12 to 15 carbons (NEODOL 25-35).

LAS is an alkyl benzene sulfonate sodium salt wherein the alkyl portion is 12 carbon atoms.

The ratios shown are by weight of the respective ingredients.

The first column of Table II shows the surfactant without the enzyme present whereas the second column shows the added cleaning power of the

enzyme. The last column shows the units of cleaning due to the enzyme.

TABLE II

| Surfactant | | Reflectance Units w/o Enzyme | + Enzyme | Units Due to Enzyme |
|---|---|---|---|---|
| APG | | 10.6 | 19.1 | 8.5 |
| LAE | | 11.9 | 15.5 | 3.6 |
| LAES | | 29.8 | 33.8 | 4.0 |
| LAS | | 28.5 | 36.1 | 7.6 |
| APG/LAES | 1:14 ratio | 16.4 | 37.1 | 20.7 |
| " | 1:6.5 | 18.6 | 40.5 | 21.9 |
| " | 1:3.9 | 23.1 | 35.7 | 12.6 |
| " | 1:3 | 22.1 | 38.5 | 16.4 |
| " | 3:1 | 21.6 | 32.8 | 11.2 |
| " | 1:1 | 27.6 | 36.6 | 9.0 |
| APG/LAE/LAES | 1:1:2 ratio | 17.0 | 33.9 | 16.9 |
| " | 1:2:1 | 20.1 | 28.3 | 8.2 |
| " | 2:1:1 | 19.4 | 32.5 | 13.2 |
| " | 1:1:6 | 27.8 | 38.3 | 10.5 |
| " | 6:1:6 | 18.2 | 27.8 | 9.6 |
| APG/LAE | 1:1 ratio | 10.5 | 18.7 | 8.2 |
| " | 3:1 | 12.3 | 20.1 | 7.8 |
| APG/LAS | 3:1 ratio | 22.6 | 29.8 | 7.2 |

Conditions:

Surfactant level - 1.4925g/l
Enzyme level - 0.0075g/l
Wash Temp - 120°F
Water hardness - 150 ppm calc. as $CaCO_3$
pH adjusted to 8.0 using $NaHCO_3$

WHAT IS CLAIMED IS:

1. A detergent composition comprising:
   (a) from about 1% to about 70% by weight of a glycoside surfactant;
   (b) from about 0.005% to about 5% by weight of an enzyme; and
   (c) from about 5% to abut 80% by weight of a member selected from the group consisting of water, lower alcohols, glycols, detergent builders and mixtures thereof.

2. The detergent composition of claim 1 wherein the average degree of polymerization of the glycoside is from about 1.2 to about 8:0

3. The detergent composition of claim 1 wherein the glycoside is selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof.

4. The detergent composition of claim 1 containing from about 3% to about 40% by weight of an anionic cosurfactant.

5. The detergent composition of claim 1 containing from about 5% to about 40% by weight of a nonionic cosurfactant.

6. The detergent composition of claim 1 containing from about 1% to about 30% by weight of cationic cosurfactant.

7. The detergent composition of claim 1 containing from about 5% to about 50% by weight of the glycoside.

8. The detergent composition of claim 2 wherein the average degree of polymerization of the glycoside is from about 1.3 to about 5.

9. The detergent composition of claim 3 wherein the glycoside is a glucoside.

10. The detergent composition of claim 1 wherein the enzyme is a protease.

11. The detergent composition of claim 1 wherein the enzyme is an amylase.

12. The detergent composition of claim 4 wherein the anionic cosurfactant is selected from the group consisting of alkyl sulfates, alkylether sulfates, olefin sulfonates, paraffin sulfonates, alkylbenzene sulfonates, and mixtures thereof.

13. The detergent composition of claim 1 wherein the glycoside contains a pendant alkoxy group.

14. The detergent composition of claim 13 wherein the glycoside is a glucoside.

15. The detergent composition of claim 14 wherein the alkoxy group is an ethoxy group.

16. The detergent composition of claim 1 in the form of a pourable liquid.

17. The detergent composition of claim 1 in the form of a granule.

AMENDED CLAIMS
[received by the International Bureau on 23 April 1986 (23.04.86);
original claims 1-17 replaced by new claims 1-15 (2 pages)]

1. A detergent composition comprising:
   (a) from about 1% to about 70% by weight of a glycoside surfactant and from about 3% to about 40% by weight of an alkyl ether sulfate surfactant;
   (b) from about 0.005% to about 5% by weight of a protease enzyme; and
   (c) from about 5% to about 80% by weight of a member selected from the following: water, lower alcohols, glycols, detergent builders and mixtures thereof.

2. The detergent composition of claim 1 wherein the average degree of polymerization of the glycoside is from about 1.2 to about 8.0

3. The detergent composition of claim 1 wherein the glycoside is selected from the group consisting of fructoside, glucoside, mannoside, galactoside, taloside, guloside, alloside, altroside, idoside, arabinoside, xyloside, lyxoside and riboside and mixtures thereof.

4. The detergent composition of claim 1 wherein the alkyl ether sulfate surfactant is a linear alcohol ethoxysulfate surfactant.

5. The detergent composition of claim 1 containing from about 5% to about 40% by weight of a nonionic cosurfactant.

6. The detergent composition of claim 1 containing from about 5% to about 50% by weight of the glycoside.

7. The detergent composition of claim 2 wherein the average degree of polymerization of the glycoside is from about 1.3 to about 5.

8. The detergent composition of claim 3 wherein the glycoside is a glucoside.

9. The detergent composition of claim 1 wherein the protease enzyme is a serine protease.

10. The detergent composition of claim 1 wherein the protease enzyme is of bacterial origin.

11. The detergent composition of claim 1 wherein the glycoside contains a pendant alkoxy group.

12. The detergent composition of claim 11 wherein the glycoside is a glucoside.

13. The detergent composition of claim 12 wherein the alkoxy group is an ethoxy group.

14. The detergent composition of claim 1 in the form of a pourable liquid.

15. The detergent composition of claim 1 in the form of a granule.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00464

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.4 C07H 3/00, 15/04; C11D 1/66, 3/386
U.S. CL. 252/174.12, 174.17

## II. FIELDS SEARCHED

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| U.S. | 252/174.12, 174.17 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [5]

## III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| X | US, E, 4,483,780 PUBLISHED 20 NOVEMBER1984 LLENADO | 1-17 |
| X | US, E, 4,493,773 PUBLISHED 15 JANUARY 1985 COOK ET AL | 1-17 |
| Y | US, A, 3,519,570 PUBLISHED 07 JULY 1970 McCARTY | 1-17 |

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

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## IV. CERTIFICATION

| Date of the Actual Completion of the International Search [2] | Date of Mailing of this International Search Report [2] |
|---|---|
| 04 APRIL 1986 | 14 APR 1986 |
| **International Searching Authority [1]** | **Signature of Authorized Officer [20]** |
| ISA/US | Dennis L. Albrecht |